# McCrone Analysis of COT Wire

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**A visit was made to McCrone Associates, Inc on Tuesday March 30, 2004 to analyze deposits of COT wires. Our primary host was Wayne Niemeyer. Kent Rhodes did the XPS analysis and Gretchen did the FTIR analysis**

**The following samples approximately one inch long were analyzed:**

- **A length of new wire (from spool).**
- **A length of aged wire from SL2_S0 (z=100-105cm).**
- **A length of aged wire from SL4_S6 (z=100-110cm)**
- **A length of wire from SL4_P8 (z=100-110cm).**
- **colored piece and a dark purple discolored piece. Strands of copper wool from the filters that included a bright copper**

**EDS RESULTS FROM WIRE SAMPLES**

**(Using JXA-8900RL)**

**The first test done was Energy Dispersive Spectroscopy (EDS) which scans the sample with an electron beam micro-probe. The electron beam ejects electrons from inner shells of the atoms and the energy of the x-rays generated when these vacant states are refilled give an indication of the elemental makeup of the sample. (Note: WDS is similar except that it measures the wavelength of the photon with a diffraction grating type technique giving a higher resolution for a more limited energy range.)**

**New wire sample showed primarily the gold coating. Analyzed with a 10keV electron beam the atomic percentages were:**

- **32.1% carbon (2.9% by weight)**
- **65.4% gold (96.8% by weight).**

**There was carbon on all the samples which at this low level was thought to be mostly background. A few dust particles were seen that contained elements. At 30keV the electron beam could see the tungsten.**

**The sample of SL2_S0 wire showed a fairly uniform coating. With a 5keV electron beam it showed the following atomic percentages:**

- **89.6% carbon**
- **4.2% oxygen**
- **6.1% gold**

**With a 10keV electron beam the elemental makeup was:**

- **83.1% carbon**
- **4.5% oxygen**
- **11.8% gold**

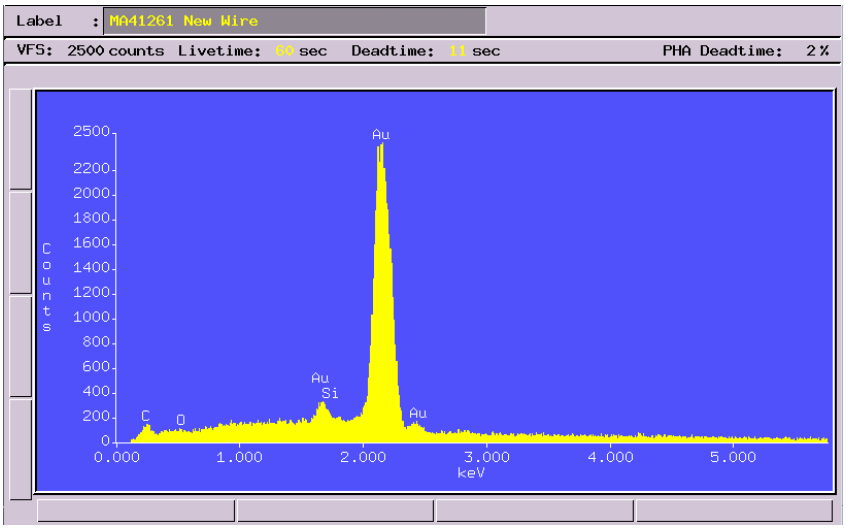


**Figure 1 EDS spectrum for a new wire at 10keV. Mostly Au with a little C. Insignificant O and Si.**

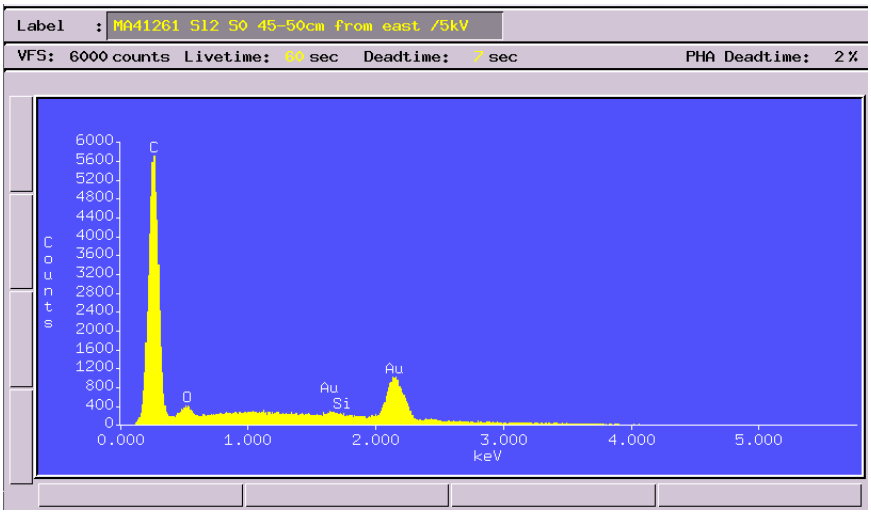


**Figure 2. EDS x-ray spectrum of SL2_S0 wire at 5keV. Mostly C with some O and Au.**

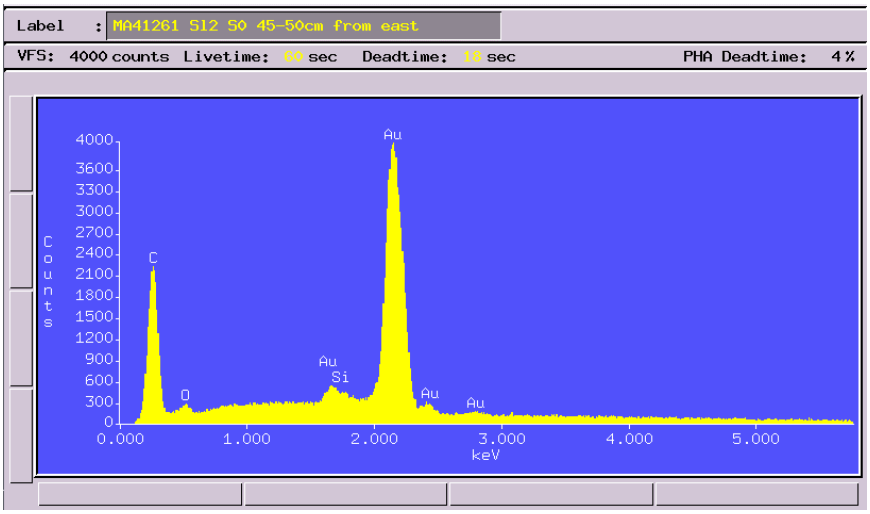


**Figure 3 EDS spectrum for SL2_S0 wire at 10keV. Higher energy electrons see more Au.**

**There were many 2-3 micron wide nodules apparent on the coating of SL2_S0 and when they were analyzed, the measured percentage of carbon increased. At 10keV electron energy, two nodules measured:**

- **93.1% and 92.9% carbon**
- **4.1% and 3.3% oxygen**
- **2.8% and 3.7%gold**

**The sample of SL4_P8 looked similar to new wire. This wire had some nodules with 70-75% carbon, but many were clearly dust or dirt with silicon, oxygen, carbon, sodium, calcium, etc. The elemental makeup of a general area measured:**

- **34.3% carbon**
- **2.3% oxygen**
- **63.0% gold.**
- **at 10keV.**

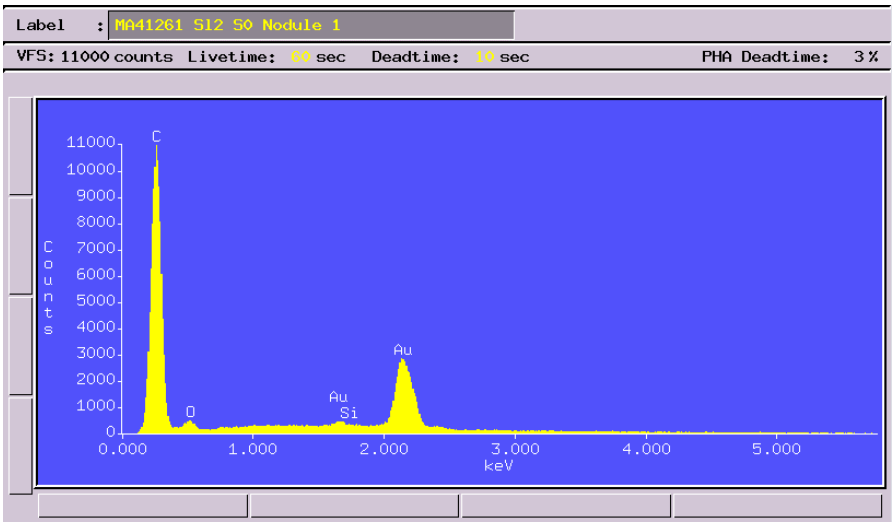


**Figure 4 EDS spectrum for nodule 1 on SL2_S0 wire at 10keV. More C and O seen,**

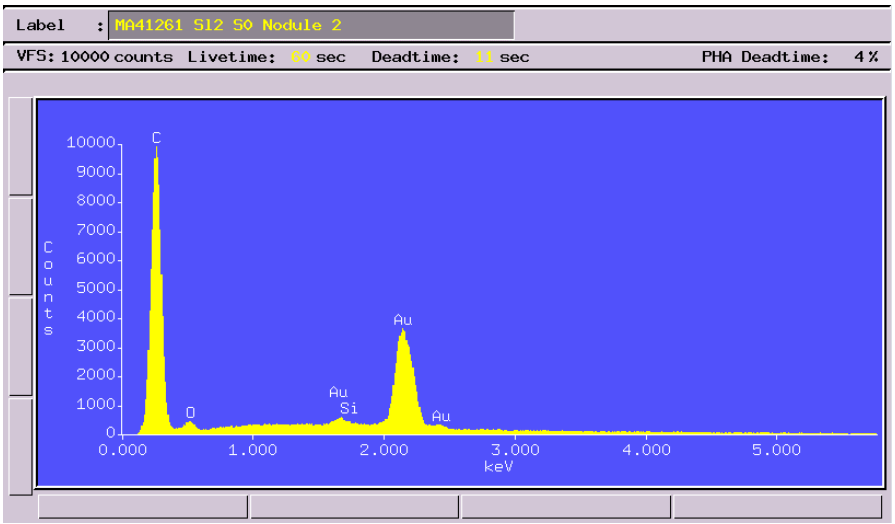


**Figure 5 EDS spectrum for nodule 2 on SL2_S0 wire at 10keV. Similar to figure 4.**

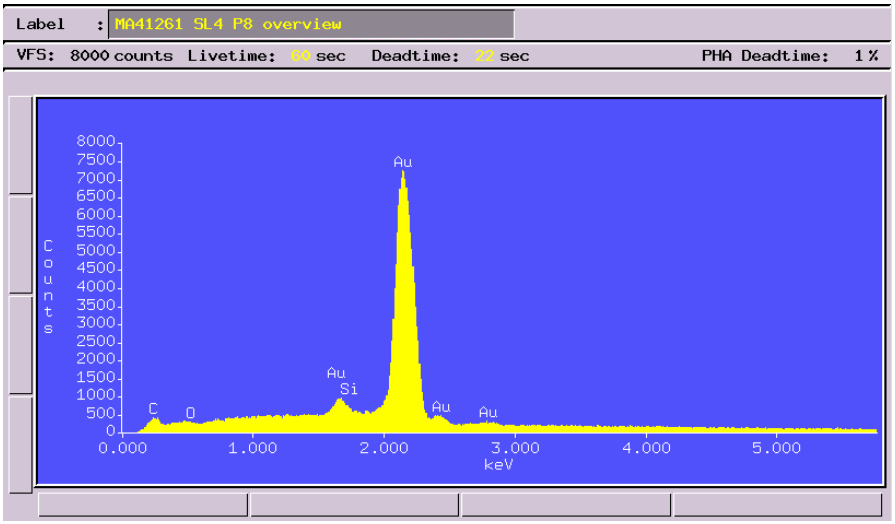


**Figure 6 EDS spectrum for SL4_P8 wire at 10keV. Similar to new wire with mostly Au and a little C.**

**The SL4_S6 wire showed a fairly uniform coating similar to SL2_S0, but with fewer nodules. The spectrum for an overview area was probed with a 10keV electron beam. The percentage atomic makeup suggested that the coating was thinner than for the SL2_S0 wire (83% C and 11,8% Au):**

- **81.4% carbon**
- **1.5% oxygen**
- **17.1% gold**

**We found a large bright spot (compared to nodule sizes) that was consistent with no coating (probably knocked off in handling):**

- **35.8% carbon**
- **1.8% oxygen,**
- **.9% silicon**
- **60.9% gold**

**There was a nodule that was measured as having less carbon the the general area measurement.**

- **73.8% carbon**
- **1.9% oxygen**
- **24.3% gold**

**Again there were spots that looked more like dust. The spectrum for one is shown in figure 10 where Cr, Fe, Ni, and Si are seen.**

**Silicon content wasn't generally listed above for two reasons. There is extremely little of it in all the COT wire samples, and at that level it can be confused with some slight sensitivity to W. For completeness, atomic % of silicon is listed here for the above samples along with their sigma in % of the reading: New Wire 10kV, 0.14% (sigma=52%); SL2_S0 5kV, 0.12% (62%); SL2_S0 10kV, 0.57% (20%); SL2_S0 nodule 1 10kV, 0.04% (54%); SL2_S0 nodule 2 10kV, 0.08% (29%); SL4_P8 10kV, 0.36% (53%); SL4_S6 10kV, 0.05% (115%); SL4_S6 bright spot 10kV, 0.89% (20%); SL4_S6 nodule, 0.04% (218%).**

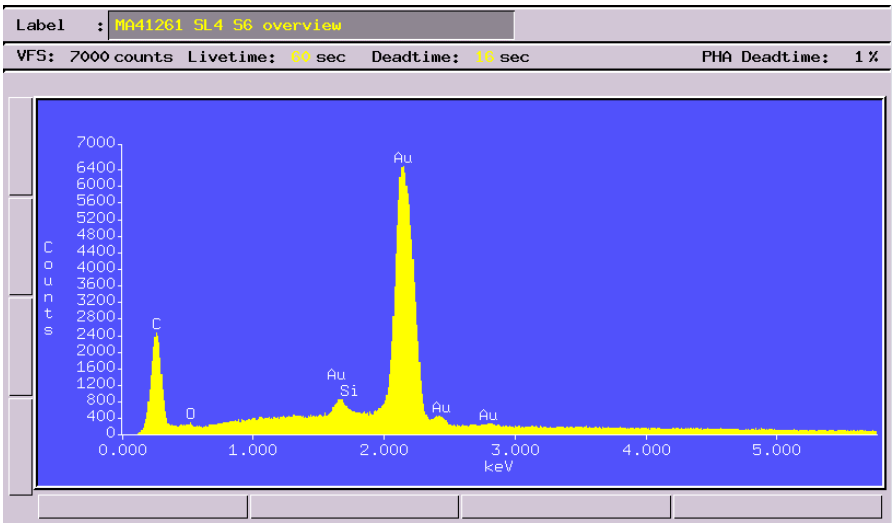


**Figure 7 EDS spectrum for SL4_S6 wire at 10keV. Similar to SL2_S0 wire but with thinner coating.**

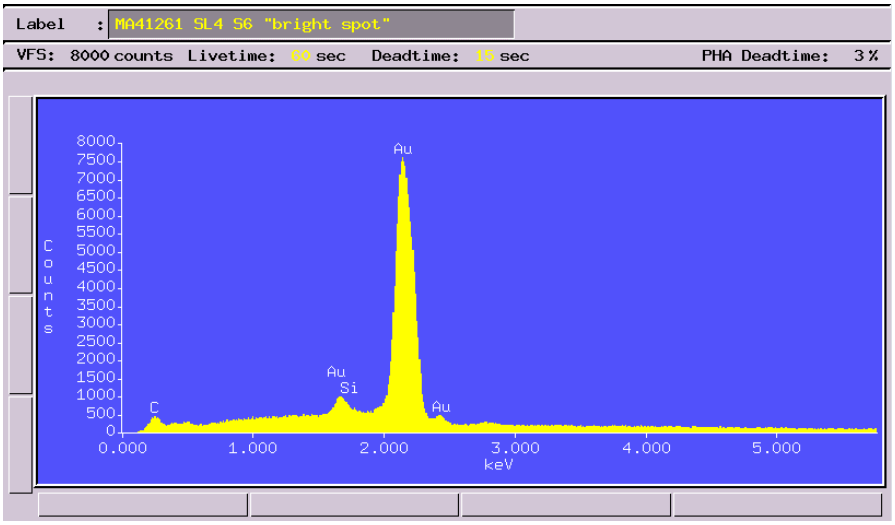


**Figure 8 EDS spectrum for SL4_S6 wire at 10keV. Taken at bright spot, looks similar to a new wire.**

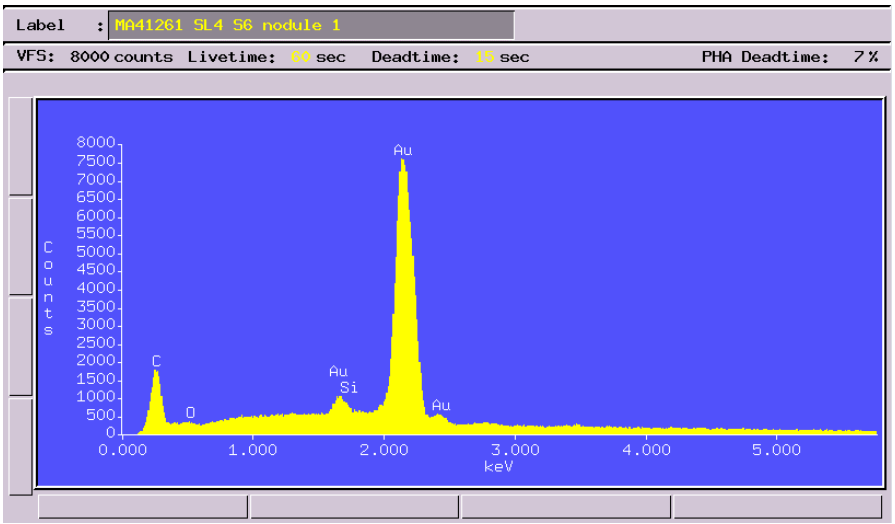


**Figure 9 EDS spectrum for SL4_S6 nodule at 10keV. Similar to the general coating.**

**The copper wool strands were also examined with EDS. Strands with little or no discoloration probed with at 10keV electron beam showed:**

- **15-18% carbon**
- **5-8% oxygen**
- **74-80% copper**

**The spectrum from a dark strand is shows a surprising amount of carbon. We had expected to find a copper oxide.**

- **57.0%**
- **8.0% oxygen**
- **34.8% copper**

**at 10keV. It was surprising that the main contaminant was carbon instead of oxygen.**

## Surface Pictures Using EDS Electron Probe

**Using the EDS electron probe, a picture of the wire surface can be determined by looking at the secondary x-rays or backscattered electrons and correlating their intensity with the electron beam position during the scan. Looking at the backscattered electrons gives a picture where low Z material comes out dark and high Z material is bright. Dark nodules were particularly prevalent on SL2_S0 using this technique.**

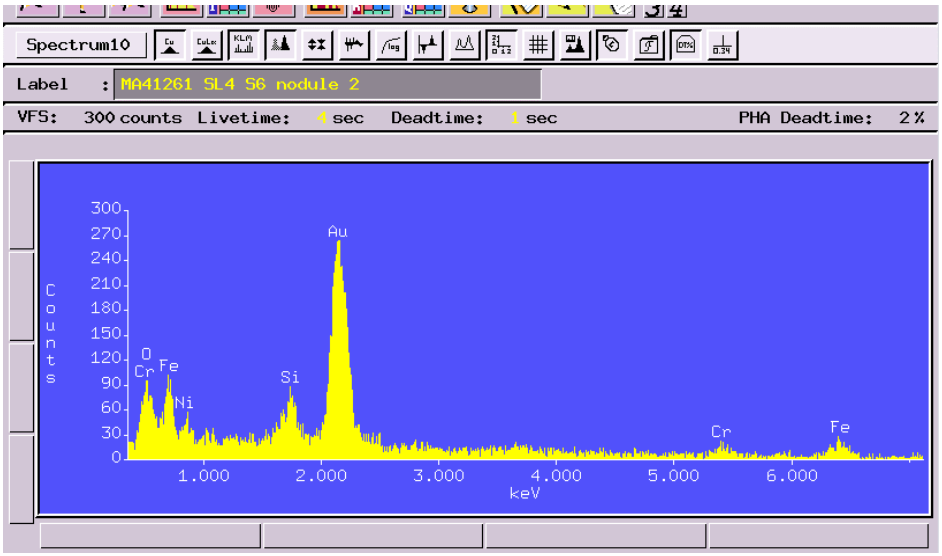


**Figure 10 EDS spectrum for SL4_S6 nodule at 10keV. This is probably a dirt speck.**

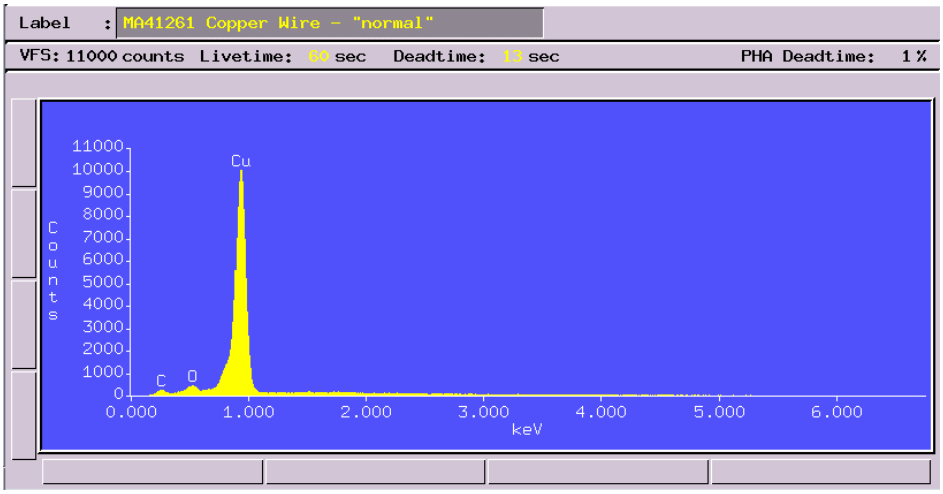


**Figure 11. EDS spectrum for a bright copper strand taken from copper wool filter.**

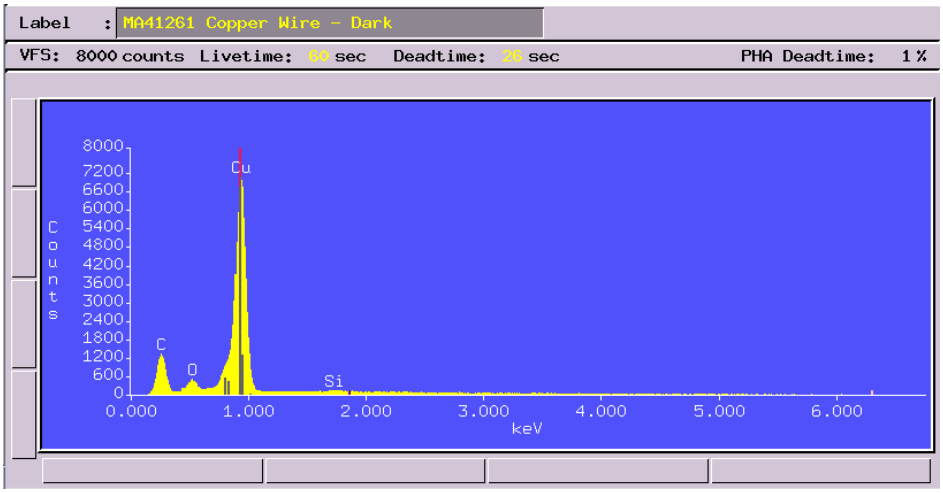


**Figure 12. EDS spectrum from dark copper stand. It has significant amounts of C.**

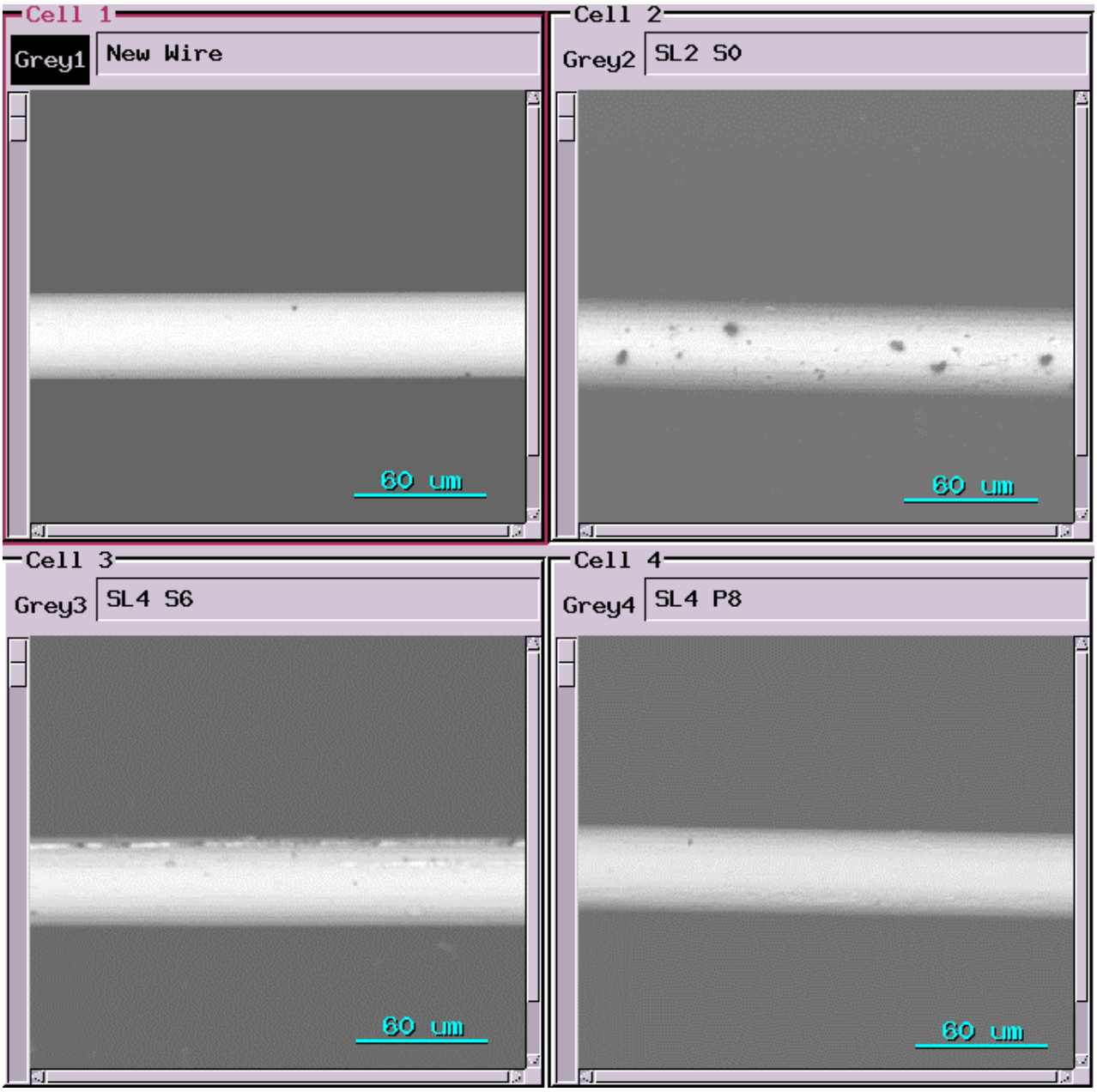


**Figure 13. Pictures form the different wire samples using backscattered electrons from the EDS probe. In these pictures, areas of low Z appear darker and areas of high Z appear brighter.**

# XPS SCANNING TO GET MOLECULAR BONDS

**The XPS measurement irradiated the samples with 1400eV x-rays and an energy scan was made of the secondary electrons emitted. A complete scan is done to get a survey of all the elements in the sample and then a precision scan is made of a small energy region to get information on the molecular bonds. This technique only probes the first few nmeters of the sample.**

- **The new wire had high gold content with a trace of carbon and oxygen. The spectrum indicated 62.0% C1s, 21.0% O1s, 15.9% Au4f, and 1.1% NaKLL.**

- **The SL2_S0 wire had large oxygen and carbon peaks with no gold. The measured amounts were 80.8% C1s, 18.8% O1s, 0.4% NaKLL.**

**Kent Rhodes indicated that the carbon and oxygen traces at this level could be absorbed from airborne species or may possibly be some residual from the wire drawing process, gold was not expected to be seen.**

**A high resolution scan was done in the region of the C1s peak on the SL2_S0 wire. The results of the precision scan were given in units of %Area. The scan found 82% CC,CH; 14% C-O; and 3%C=O. The C-O percentage was significant and the oxygen presumably comes from the alcohol**

**The XPS apparatus can also be used to etch away the surface area with singly charged argon ions. The energy can be varied from a few hundred eV to a few keV. A thickness of about 5 nmeters was etched away from our sample using 500eV argon ions. This is primarily an attempt to make sure that we are not measuring surface contamination. The results were 88% CC, CH; 10% C-O, and <1% for C=O.**

**Kent noted that if one used Auger electrons to probe the surface instead of X-rays, one could get a similar analysis of a small point on he surface, such as one of the nodules. The XPS focus is about 20 microns, half the diameter of the wire.**

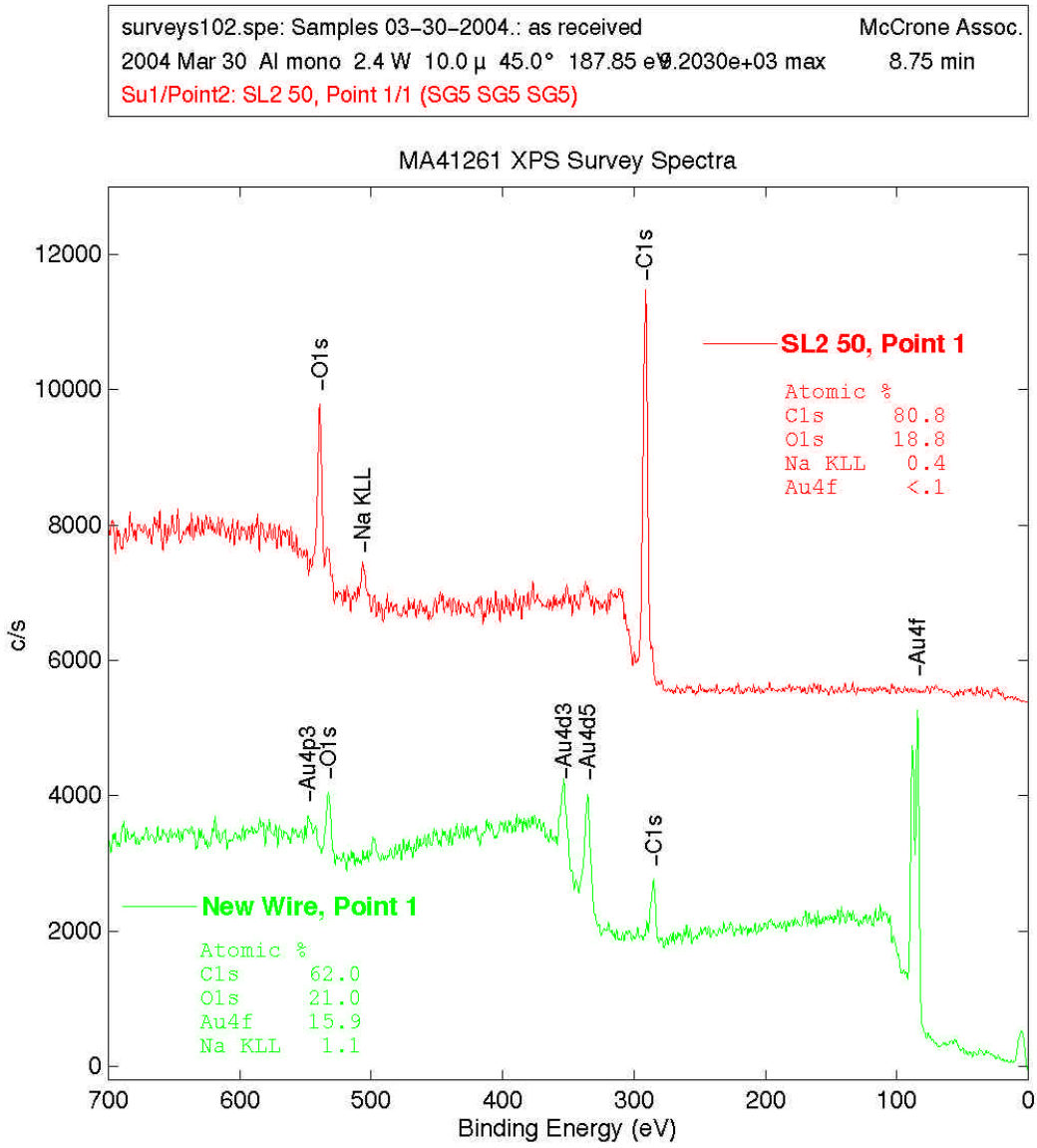


**Figure 14. The broad energy spectra from a new wire sample and SL2_S0 sample using XPS analysis. The green is for the new wire and the red is for the SL2_S0 sample. The x-ray from the XPS probe only penetrate a few nmeters.**

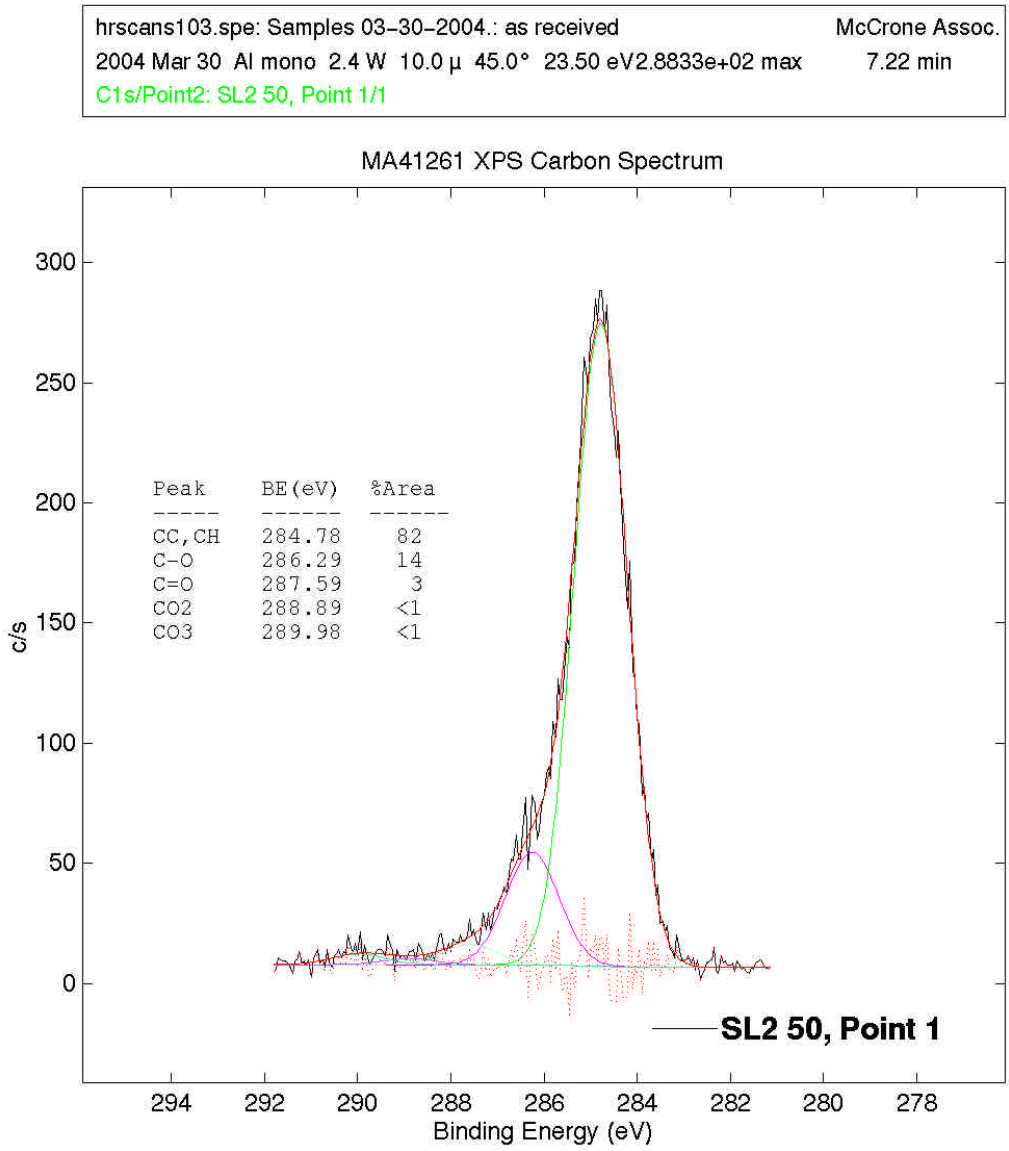


**Figure 15. Precision XPS scan of the C1s peak on SL2_S0 wire sample. Considerable C-O bonds are present in the shoulder.**

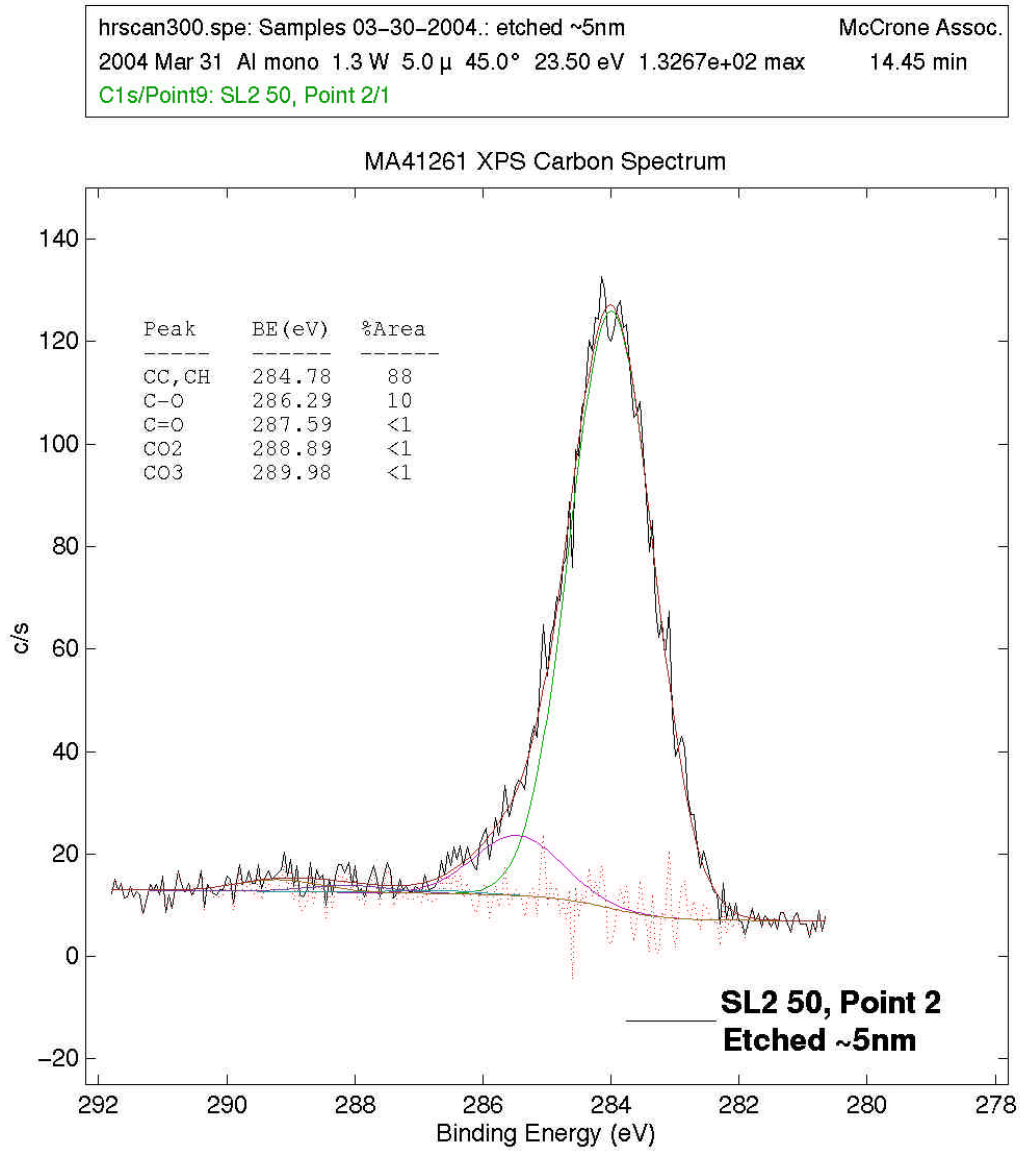


**Figure 16. Precision XPS scan of the C1s peak on SL2_S0 wire sample after etching away about 5 nmeters of surface material using an argon ion beam. The C=O bonds are no longer apparent.**

# FESEM HIGH RESOLUTION PICTURES OF THE SURFACE

# (JSM-6301FXV)

**Field Effect Secondary Emission Scanning (FESEM) uses an electron beam making it similar to the EDS analysis. However in this instrument, the electron beam starts from a point field emission source producing a very narrow, well defined electron beam. Secondary electrons are monitored to give a high spatial resolution picture of the surface features.**

**Several pictures were made:**

- **The first shows a sample of new wire.**
- **The second shows the coating on a typical region of the SL2_S0 sample with lots of sub-micron nodules.**
- **The third shows a relatively rare larger nodule.**
- **The fourth shows a scraped area of the SL2_S0 wire. In the foreground the bare wire can be seen; behind this area is a smooth dark coating about 300 nmeters thick with lots of sub-micron nodules. The background at the top of the picture is the black tape that was used to secure the sample.**
- **The fifth shows a general shot of SL6_S4. There are more striations apparent than for SL2_S0 indicating a thinner coating. Also fewer nodules.**
- **The sixth shows SL6_P8 where there appears to be a lot of dark "dirt" type paticles. (Wayne had trouble mounting this wire and it may have taken quite a beating.) In general, the surface looked similar to the new wire.**
- **The Cu strands had so many striations that it was difficult to analyze the FESEM pictures.**

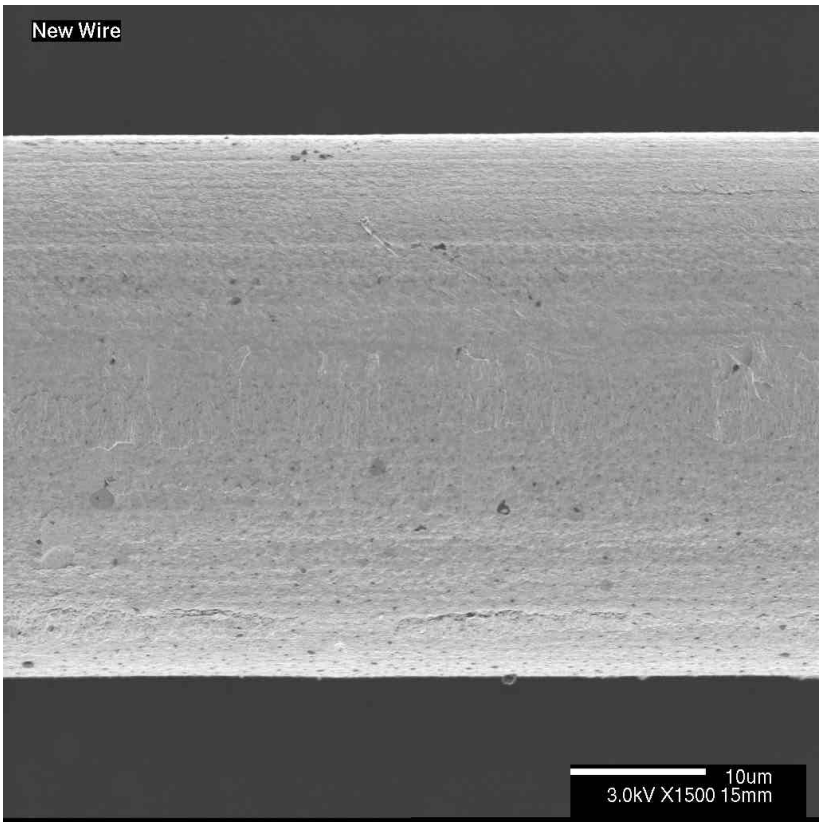


**Figure 17. FSEM high resolution picture of a new wire using a precision electron beam.**

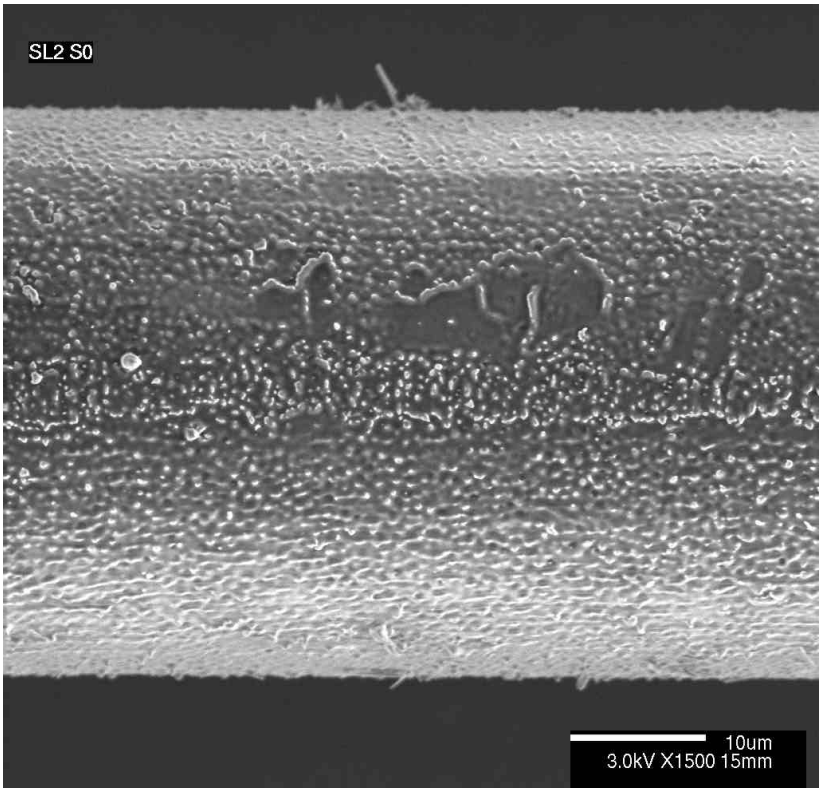


**Figure 18. FESEM high resolution picture of SL2_S0. Lots of sub-micron nodules are seen.**

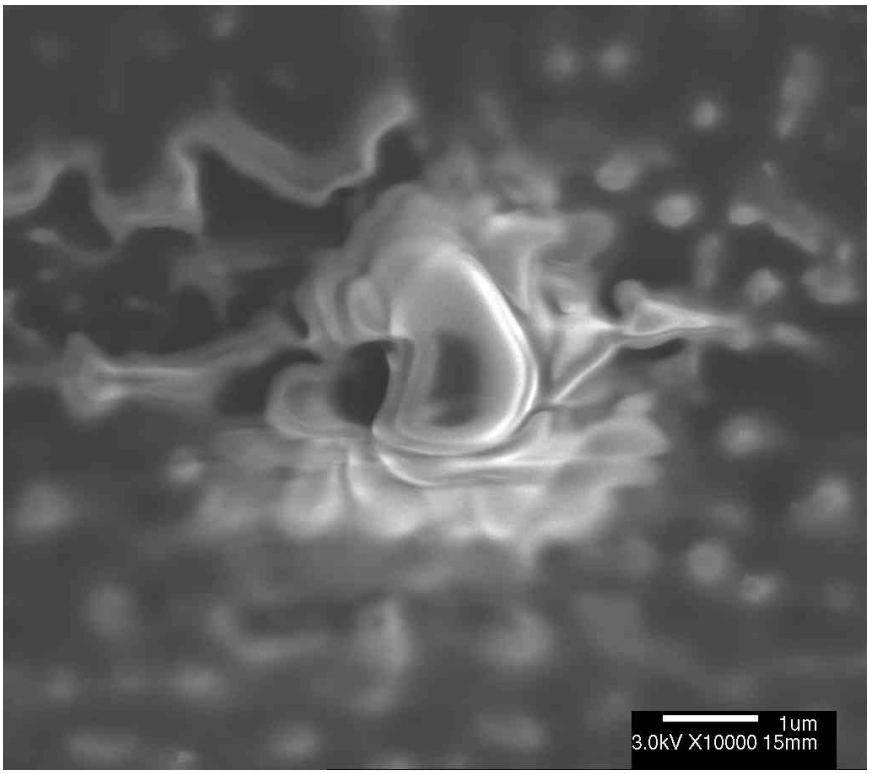


**Figure 19. FESEM high resolution picture of SL2_S0 showing a large nodule.**

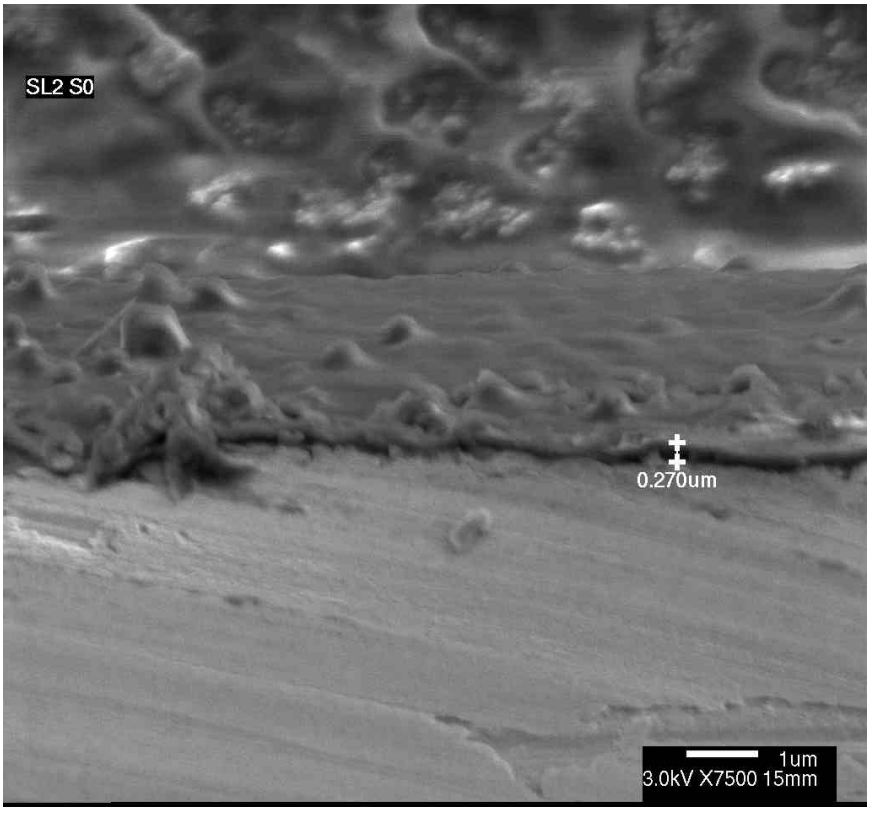


**Figure 20 FESEM high resolution picture of SL2_S0. In the foreground the coating has been scraped off revealing bare wire. The dark coating with nodules is about 270 nm thick. In the background is tape.**

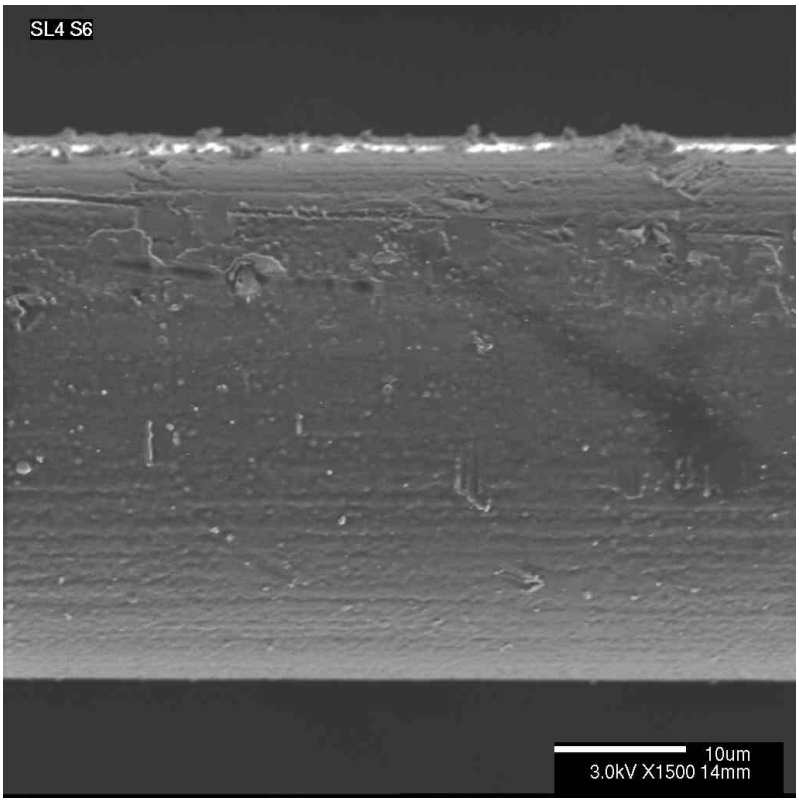


**Figure 21 FESEM high resolution picture of SL4_S6. Thinner coating has fewer nodules.**

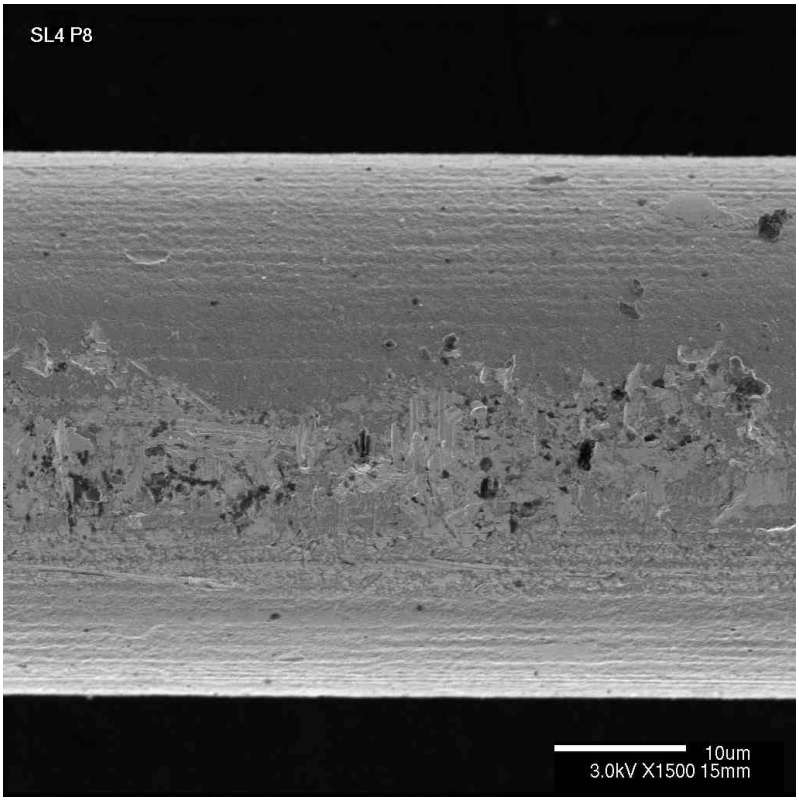


**Figure 22. FESEM high resolution picture of SL4_P8. A dirty section of the wire is shown.**

# FTIR ANALYSIS

**Fourier Transform Infrared analysis was done on the SL2_S0 wire to learn more about the molecular makeup of the coating. This type of reflection spectroscopy irradiates the sample with a broadband infrared beam. The surface is penetrated a short distance by the infrared rays and the reflected spectrum is examined for dips associated with absorption by the sample. Wavenumbers from 4000 to 1000 cm-1 were analyzed.**

**A dark copper wool strand was measured first but nothing was learned, probably due to the rough nature of the surface.**

**The reflected spectrum for the SL2_S0 wire has the following features:**

- **A broad dip near 3365 cm-1 associated with the OH bond (stretching).**
- **Sharper dips at 2958, 2931, and 2870 cm-1 associated with CH2 and CH3 bonds.**
- **Two small dips near 2300 cm-1 probably associated with background CO2.**
- **Two small dips at 1734 and 1698 cm-1 associated with the C=O bond.**

**There was considerable ringing in the system for wavenumbers beyond 2000 cm-1, so it was difficult to tell what was happening in this region.**

**Simple aliphatic hydrocarbon strings (either straight or branched) have no oxygen, so what we have appears to be more complicated. (The OH bond is found in water or alcohol samples).**

**Although the CH and OH bonds are found in our drift gas mixture, they could conceivably be from a contaminant, such as an aliphatic oil.**

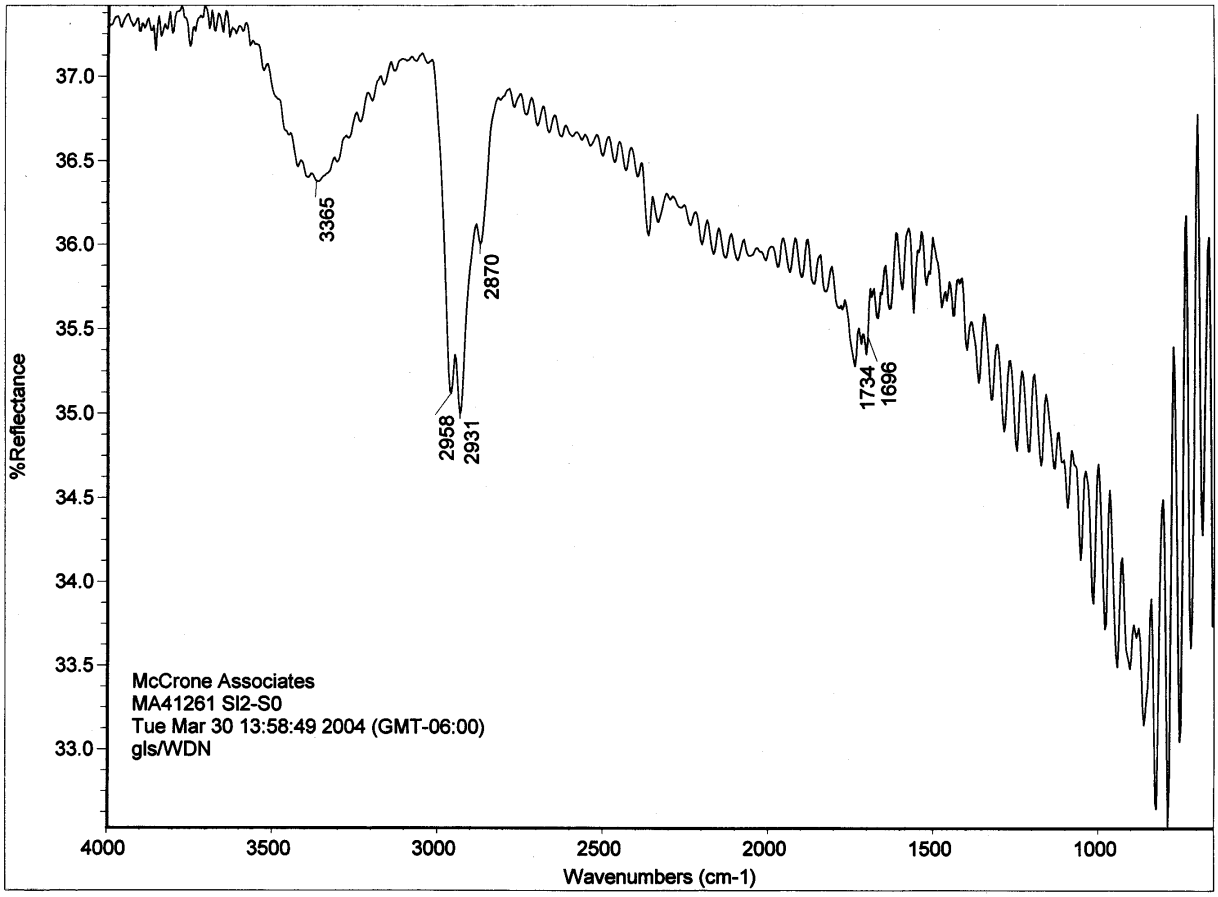


**Figure 23. FTIR spectrum showing the absorption bands in reflected infrared light associated with molecular bonds. The broad dip at 3365 is the OH (stretching) bond. The dips at 2958, 2931, and 2870 are the CH2 and CH3 bonds. Two small dips at about 2300 are probably background CO2. The dips at 1734 and 1696 are probably C=O bonds.**

# RAMAN ANALYSIS

**An attempt was made to do Raman analysis on our SL2_S0 sample. In Raman analysis, the sample is irradiated with a laser beam and the inelastically scattered light spectrum is analyzed for evidence of the excitation of molecular states. In our case too much background fluorescence prohibited identification of surface compounds.**